AB Using a newly developed method with which surface parameters of metals, such as surface energy and surface diffusion coeff. of **adatoms**, can be measured from the change of surface morphol., the effect of H adsorption on the crystal sizes formed in **galvanostatic** electrodeposition was studied. As a result, the reasons for the eccentric formation of minute, powdery crystals accompanied by H evolution were derived as follows: because surface diffusion of metal **adatoms** is strongly hindered due to satd. adsorption of H atoms, the supersatn. of the **adatoms** is violently promoted. Many small crystals resulting from nucleation growth, therefore, continuously appear at high growth velocity. At the same time, the surface energy of the crystals also increases and its value is mainly detd. by adsorbed H, so that the tendency for rapid formation of minute crystals is greater. On the other hand, when H adsorption can be disregarded, crystals grow more slowly and are relatively larger. The transition from a H-nonadsorbed state to a H-adsorbed state is rather discontinuous; immediately after the electrode surface is covered with H, the crystals suddenly become reduced in size.

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=> d his

(FILE 'HOME' ENTERED AT 23:14:33 ON 06 DEC 2007)
FILE 'CA' ENTERED AT 23:14:41 ON 06 DEC 2007
E BOCKRIS J/AU
L1 250 S E4-13 AND PY<1968
L2 2 S L1 AND ADATOM?
L3 19 S L1 AND GALVAN?
L4 31 S L1 AND (SILVER OR AG)
L5 42 S L2-4

=> d bib,ab l5 1-42

L5 ANSWER 17 OF 42 CA COPYRIGHT 2007 ACS on STN
AN 55:58241 CA
OREF 55:11136f-i,11137a
TI Calculation of potential energy profile diagrams for processes in electrolytic metal deposition
AU Conway, B. E.; **Bockris, J. O'M.**
CS Univ. Ottawa, Can.
SO Electrochimica Acta (**1961**), 3, 340-66
AB Neutralization of the transferred ions to form adsorbed metal atoms is distinguished from ion-transfer processes in which the transferred entity maintains ionic character, with the appropriate no. of stoichiometric electrons entering the metal lattice for each ion transferred. The elementary processes considered are: transfer of ions from the soln. to different types of surface sites on the metal; surface diffusion of adsorbed ions; successive dehydration of the adsorbed ions in lattice building. The free energies of the transition states in successive steps in consecutive ion-transfer, surface-diffusion, and lattice-building reactions are compared. The probable rate-detg. process is deduced for deposition of Cu++, Ni++, and **Ag**+ on the resp.

metals. The heat of activation ΓH0* for transfer of ions from the soln. to the metal surface depends on the site to which transfer occurs, that for a planar site being significantly less than that for other sites (e.g. edges, kinks, etc.). Transfer to form completely nonpolar neutral **adatoms** has prohibitively high values of ΓH0*. Direct deposition of Cu++ on to surface sites would involve a very high ΓH0*. The path Cu++ + eM → Cu+ followed by Cu+ + eM → (Cu+adion + eM) is assocd. with ΓH0* values significantly lower than that of direct Cu++ deposition. The free-energy diagrams are consistent with a rate-detg. redn. mechanism found exptl. Near the Cu/Cu++ reversible potential the free-energy barrier for adion surface diffusion can become the highest, which is consistent with observations under these conditions. With **Ag**+ deposition the ion-transfer step has the highest free-energy barrier at high neg. overpotentials, whereas near the reversible potential the barrier for surface diffusion can become the highest. The kinetic behavior found exptl. with **Ag** supports the theoretical conclusions. The low exchange c.d. for Ni++ deposition is probably assocd. with the instability of the simple Ni+ ion in aq. soln.

L5 ANSWER 20 OF 42 CA COPYRIGHT 2007 ACS on STN
AN 54:85302 CA
OREF 54:16222b-d
TI Kinetics of the deposition and solution of **silver**
AU Despic, A.; **Bockris, J. O'M.**
CS Univ. of Pennsylvania, Philadelphia
SO Journal of Chemical Physics (**1960**), 32, 389-402
AB **Galvanostatic** measurements, made on spherical **Ag** electrodes in. purified aq. acid solns. of AgClO4 at c.ds. up to 10 amp./sq. cm., yielded overpotential as a function of time and faradaic c.d. at const. total current. Variables were total c.d., concn. of **Ag** ions, and state of the electrode surface. The theory of the surface diffusion kinetics was developed to encompass regions of high c.d. and the surface ad-ion concn. was evaluated. A theoretical analysis of the steady state of surface diffusion control of the metal-ion exchange reaction indicated that the current is distributed nonuniformly between growing sites, with const. potential over the electrode surface. The symmetry factor β of electrode kinetics is potential dependent, and, in systems of sufficiently high i0 values, tends towards zero at high overpotential. This fact results in a limiting c.d. for a transfer-controlled process. The tendency towards such a current was observed.

L5 ANSWER 25 OF 42 CA COPYRIGHT 2007 ACS on STN
AN 53:104142 CA
OREF 53:18684e-h
TI The mechanism of electrolytic deposition and dissolution of **silver**
AU Mehl, Wolfgang; **Bockris, John O'M.**
CS Univ. of Pennsylvania, Philadelphia
SO Canadian Journal of Chemistry (**1959**), 37, 190-204
AB cf. C.A. 52, 1811b; 53, 3937b. The **galvanostatic** method with short-time (millisec.) polarization was used in the measurement of the current-

potential curves for **Ag** in highly purified AgClO4-HClO4 solns. over a range of c.ds. from 0.3 ma./sq. cm. to 0.8 amp./sq. cm. Thermally etched **Ag** electrodes were prepd. in a spherical shape by partial melting of **Ag** wire, 0.5 mm. in diam., in a purified H atm. Electron micrographs showed etch pits at a d. of about 10 amp. sq. cm., indicating dislocations with a screw component normal to the surface. Analysis of the data, accounting for double layer charging, diffusion of ions, and steady state relations, shows that at low overpotentials the principal rate-detg. step is the surface diffusion of adions. At high over potentials the rate-detg. step is the transfer of ions from solns. to electrode. It is predicted that this is true down to **Ag**+ concns. of about 10-4 mole/l. The transition from rate-detg. surface diffusion to rate-detg. transfer is due to the decrease in average distance between growing lines and hence increase in the surface diffusion flux with increasing over potential. The equil. concn. of adions during electrochem. deposition is very much higher than the equil. concn. of **adatoms** during deposition from the vapor phase. At higher overpotentials, about 100 mv., there is poor reproducibility. Superpolarization was observed almost exclusively for solns. which had not been well purified.

L5 ANSWER 30 OF 42 CA COPYRIGHT 2007 ACS on STN
AN 52:10271 CA
OREF 52:1811b-c
TI Mechanism of electrolytic **silver** deposition and dissolution
AU Mehl, W.; **Bockris, J. O'M.**
CS Univ. of Pennsylvania, Philadelphia
SO Journal of Chemical Physics (**1957**), 27, 818-19
B **Galvanostatic** expts. were carried out on **Ag** electrodes in solns. of AgClO4 in HClO4. The shape of the c.d.-over-voltage curve at low c.ds. was consistent with the assumption that a slow diffusion step occurs after transfer of the ions to the surface of the electrode. At overvoltages in excess of 60 mv., the rate-controlling step is the transfer of ions from the soln. to the metal.

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